

Electrophilicity and spin polarization of simple substituted silylenes

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Abstract

The philicity indices, ω_N , and ω_S^\ddagger , characterize a charge transfer process occurring at constant spin number, and the spin polarization for a process at constant number of electrons, respectively. These descriptors are explored for a series of substituted C_2HSiX silylene isomers ($X = F, Cl, Br, H$), providing new insights for a comprehensive description of global and local chemical reactivity patterns and halogen substituent effects in these systems.

1. Introduction

Silylenes are dicoordinate silicon reactive intermediates analogues of carbenes exhibiting unique properties in catalysis and stereoselective processes within synthetic organo-silicon chemistry [1,2]. Several experimental and theoretical studies have focused on their preparation, structure, singlet–triplet interplay, and the analysis of structural factors controlling their relative stabilities [3–5]. The origin of the nature of a singlet closed-shell electronic structure for the silylene ground state (GS) has attracted great attention. A singlet GS has a pair of electrons in an orbital of σ symmetry, while in the triplet state, these electrons remains unpaired occupying orbitals of π and σ symmetry [6]. The different multiplicities of the GS of the parent carbene (CH_2), and other divalent species (MR_2) containing elements of the group 14, can be understood in terms of the frontier molecular orbitals energies. The HOMO–LUMO energy gap in SiH_2 is much larger than in CH_2 , and the singlet state becomes the GS [7]. Despite the many reported experimental efforts to prepare a triplet ground state for sil-

ylene [8,9], there has been no definitive evidence for the existence of such a triplet ground state. Theoretical studies have predicted it is achievable using bulky silyl groups as appropriate substituents [10,11]. Such bulky substituents would increase the bond angle at the divalent silicon atom from the value found in SiH_2 (i.e., 92°) [12]. In silylenic systems, the potential energy curves for the lowest singlet and triplet states cross one another when the H–Si–H angle is around 130° , indicating a possibility to obtain triplet ground states [13]. In this context, Gaspar et al. [14] have photochemically generated bis-(tri-isopropyl-silyl)silylene, $(iPr_3Si)_2Si$, although unfortunately the reaction products did not establish conclusively the ground-state multiplicity. Further works have been proposed by the authors to identify the electronic GS of this silylene species [14]. In fact, Kassae et al. have recently reported four triplet GS of silylenes among thirty possible silylenic $XHSi_3$ structures ($X = H, F, Cl, Br$) at both ab initio and DFT levels. Halogen substitution plays a primary role in the modulation of reactivity in these systems [15–17].

Silylenes having singlet ground states are electrophilic species [18] and its insertion reactions into a σ -bond or addition reactions to π -bonds tends to follow a nucleophilic rearrangement pathway [5,13]. From the theoretical point of view, there has been a continuous interest in to study the singlet–triplet energies of a variety of substituted

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silylenes at ab-initio and density functional level of theory [19–21]. Structures, relative stabilities and triplet-singlet splitting of divalent compounds of the elements of the group 14 have received more attention [22,23].

A recent analysis based on the consideration of total energies, has just explored the halogen substitution effect in the stabilization of the singlet and triplet states via electron resonance conjugation or inductive electronic effects in the isomers of C_2HSiX ($X = F, Cl, Br, H$) [24]. In the present work, we show and stress that the nature of these responses could be further characterized by using global and local descriptors based on the conceptual framework of spin-polarized density functional theory (SP-DFT) [25,26]. In particular, we focus on the nature of the electrophilicity power and spin polarization proclivities [25], with the aim to provide support [24] and to examine the applicability and usefulness of recently introduced SP-DFT philicity descriptors [25,26].

2. Model equations and computational details

Electrophilicity is a powerful but elusive concept in chemistry that refers to the ability of a given system to establish a stable interaction with a source of electrons. Recently, the nature of the electrophilicity index introduced by Parr et al. [27], its wide range of applicability and predictive ability have been reviewed by Chattaraj et al. [28]. A generalized discussion of both global and local electrophilicity and nucleophilicity (i.e., philicity) was also presented by Chattaraj et al. [29] by using the normalization condition of the Fukui function. It has been stressed that this quantity contains information about structural, reactivity and selectivity patterns of many electron systems in both ground and excited electronic states [28]. By extending Parr’s derivation [27] into the SP-DFT formalism, we have recently introduced [25] an electrophilicity power at constant spin number, ω_N , as

$$-\omega_N \equiv \Delta E_{v,N_s,\max} = -\frac{(\mu_N^\pm)^2}{2\eta_{NN}}. \quad (1)$$

Additionally, the meaning of a spin-polarization index (i.e., the change of spin number at constant number of electrons), first discussed by Perez et al. [30], and Geerlings et al. [3,4,31] has been also further clarified within the framework of SP-DFT [25],

$$\Delta E_{v,N}^* = -\frac{(\mu_S^\pm)^2}{2\eta_{SS}} \equiv -\omega_S^\pm > 0. \quad (2)$$

ω_S^\pm measures the ability of a system to change its spin polarization state, as response of interaction with an electromagnetic field of suitable energy, being identified as the philicity for spin-polarization [25]. There are not electron transfer implied in the model (2) as initially claimed [4,30]. Local reactivity descriptors have been also introduced through the generalized Fukui functions [33,29], $\omega_N^\pm(\mathbf{r}) = \omega_N f_{NN}^\pm(\mathbf{r})$, and $\omega_S^\pm(\mathbf{r}) = \omega_S f_{SS}^\pm(\mathbf{r})$. $f_{NN}^\pm(\mathbf{r})$ describes

the internal charge redistribution under a process of constrained charge transfer at constant spin number, while $f_{SS}^\pm(\mathbf{r})$ measures the associated change in the spin density under a spin polarization process. The change in the electron density itself in the last case is measured via the Fukui function $f_{NS}^\pm(\mathbf{r})$ [25,32]. Operational formulas for the chemical potential and hardness quantities entering such definitions, are [25,32]

$$\begin{aligned} \mu_N^- &\approx \frac{1}{2}(\epsilon_{\text{HOMO}}^\alpha + \epsilon_{\text{HOMO}}^\beta), & \mu_N^+ &\approx \frac{1}{2}(\epsilon_{\text{LUMO}}^\alpha + \epsilon_{\text{LUMO}}^\beta), \\ \mu_N &\approx \frac{1}{2}(\mu_N^+ + \mu_N^-), & \eta_{NN} &\approx (\mu_N^+ - \mu_N^-) \end{aligned} \quad (3)$$

and

$$\begin{aligned} \mu_S^- &\approx \frac{1}{2}(\epsilon_{\text{HOMO}}^\alpha - \epsilon_{\text{LUMO}}^\beta), & \mu_S^+ &\approx \frac{1}{2}(\epsilon_{\text{LUMO}}^\alpha - \epsilon_{\text{HOMO}}^\beta), \\ \eta_{SS}^{M-M'} &\approx (\mu_S^{(M')-} - \mu_S^{(M)+})/\Delta N_S \end{aligned} \quad (4)$$

where the $\epsilon_i^{\alpha,\beta}$ stands for the i th frontier eigenvalue of a given α or β spin state. The spin hardness, η_{SS} , is evaluated for the interval (M, M') of spin multiplicities ($M < M'$) through the spin potentials $\mu_S^-(M')$ and $\mu_S^+(M)$ using the ground state geometry of multiplicity M . We note in this point that Eqs. (3) and (4) are based on the frozen core approximation. Recently a comparison between this method and the finite difference approximation, shows that they provide similar results when occupied orbitals are involved, but larger differences if virtual orbitals become implied [33]. All calculations have been carried out at the UB3LYP/6-311++G(d,p) level of theory using the GAUSSIAN 98 package of programs [34].

3. Results and discussion

Fig. 1 depicts the silylene systems studied in the present work. Table 1 reports the relevant SP-DFT quantities for these systems both in their singlet ground state and the triplet excited state as well as the corresponding vertical and adiabatic transition energy changes. We focus directly only on those recently defined SP-DFT global responses given by Eqs. (1) and (2) [25], both at constant spin number

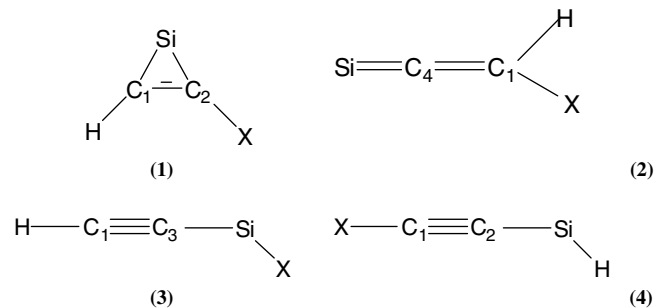


Fig. 1. C_2HXS silylene systems ($X = H, F, Cl, Br$) studied in this work: (1) silacyclopropenyldiene, (2) vinylidenesilylene, (3) propargylsilylene, and (4) ethynylsilylene.

Table 1
Singlet and triplet SP-DFT properties: chemical potential (μ_N), hardness (η_{NN}), and electrophilicity (ω_N)

	2S + 1	$\Delta E_{s \rightarrow t}^{\text{ad}}$ (kcal/mol) ^a	$\Delta E_{s \rightarrow t}^{\text{vt}}$ (kcal/mol) ^b	$\Delta E_{s \rightarrow t}^{\text{vt}}$ (kcal/mol) ^c	μ_N (eV)	η_{NN} (eV)	ω_N (eV)	μ_S^+ (eV)	η_{SS} (eV)	ω_S^+ (eV)
1H	1	72.5	72.7	72.4	-4.28	5.21	1.76	2.61	-1.04	-3.28
	3				-4.23	2.76	3.25			
1F	1	70.1	70.7	70.3	-4.48	5.05	1.99	2.52	-1.00	-3.19
	3				-4.54	3.11	3.31			
1Cl	1	60.5	71.0	70.1	-4.57	4.99	2.09	2.49	-0.97	-3.20
	3				-4.53	2.79	3.68			
1Br	1	61.0	70.8	69.1	-4.52	4.89	2.09	2.44	-0.94	-3.17
	3				-4.72	3.00	3.71			
2H	1	22.1	24.2	24.5	-4.51	2.72	3.74	1.37	-0.83	-1.12
	3				-4.60	3.31	3.20			
2F	1	34.4	38.2	38.5	-4.85	3.32	3.55	1.65	-0.82	-1.67
	3				-4.95	2.88	4.25			
2Cl	1	29.1	32.1	32.4	-4.98	3.04	4.07	1.51	-0.81	-1.41
	3				-4.99	2.87	4.35			
2Br	1	28.1	31.1	31.4	-4.95	2.96	4.14	1.47	-0.79	-1.37
	3				-4.93	2.74	4.44			
3H	1	23.9	31.6	31.5	-4.87	3.25	3.65	1.62	-0.93	-1.40
	3				-4.41	4.60	2.11			
3F	1	45.4	52.9	52.2	-5.04	4.30	2.96	2.15	-1.01	-2.27
	3				-4.77	3.85	2.96			
3Cl	1	38.7	45.9	45.4	-5.27	3.88	3.58	1.93	-0.95	-1.97
	3				-4.90	3.87	3.10			
3Br	1	36.9	44.2	43.7	-5.20	3.71	3.65	1.86	-0.91	-1.90
	3				-4.87	3.73	3.18			
4F	1	25.1	32.4	32.3	-4.82	3.28	3.53	1.63	-0.93	-1.43
	3				-4.31	4.74	1.96			
4Cl	1	24.4	31.7	31.5	-4.85	3.19	3.69	1.59	-0.90	-1.39
	3				-4.36	4.38	2.17			
4Br	1	24.2	31.5	31.3	-4.82	3.16	3.67	1.57	-0.89	-1.38
	3				-4.37	4.15	2.30			

Vertical ($\Delta E_{s \rightarrow t}^{\text{vt}}$) and adiabatic ($\Delta E_{s \rightarrow t}^{\text{ad}}$) singlet–triplet transition gaps, and spin potential (μ_S^+), spin hardness (η_{SS}), philicity for spin polarization (ω_S^+) for simple silylenes.

The (t^*) symbol stands for a triplet calculation using the geometry of the singlet (s) ground state.

$$^a \Delta E_{s \rightarrow t}^{\text{ad}} = E^{(t)} - E^{(s)},$$

$$^b \Delta E_{s \rightarrow t}^{\text{vt}} = E^{(t^*)} - E^{(s)},$$

$$^c \Delta E_{s \rightarrow t}^{\text{vt}} = (\mu_S^+ + \mu_S^{-(t^*)}).$$

(i.e., chemical potential, μ_N , hardness, η_{NN} , and electrophilicity, ω_N), and at constant number of electrons (i.e., philicity for spin polarization, ω_S^\pm , and spin hardness, η_{SS}).

3.1. Electrophilicity power

Taking X = H as reference, it can be noted from Table 1, that the global electrophilicity power, ω_N , increases along the series of silylenic systems in the order F < Cl ≤ Br in both their singlet and triplet states. For instance for system (2), such a trend (i.e., $\omega_{N,X}/\omega_{N,H}$) is 0.95 (1.33), 1.09 (1.36), and 1.11 (1.39) times, for X = F, Cl, and Br respectively, in the singlet (triplet) electronic state. This observation can be explained on the basis that the global hardness values, η_{NN} , becomes almost directly proportional to the halogen electronegativity that provides a lower stabilization of the LUMO energy as compared to the HOMO energy in these systems. Being relatively small the variation of the chemical potential μ_N along the series (i.e., 0.1–0.5 eV), such an increase in η_{NN} yields to lower ω_N values (i.e., Eq. (1)).

Such effect on global hardness decreases with the electronegativity of substituent. Note also that the triplet excited state for species (1) are predicted to have a higher electrophilic character than the singlet ground state ($\omega_{N,X}^t/\omega_{N,X}^s$) by factors of 1.85, 1.66, 1.76, and 1.78 for H, F, Cl, and Br, respectively. This fact could be explained based on a direct interaction between the halogen substituents and the aromatic ring [24]. In fact, the lower values of electrophilicity are predicted for system (1), particularly 1H in its singlet ground state. A similar trend is observed for system (2) with factors of 0.86, 1.20, 1.07, and 1.07, for H, F, Cl, and Br, respectively, with the exception of X = F, that exhibits a deactivation in the triplet state. This deactivation in the triplet global electrophilic power, as the case for simple carbene systems, is also true for the remaining silylenic systems by factors of 0.58(0.58), 1.00(0.56), 0.87(0.59), and 0.87(0.63) for H, F, Cl, and Br, respectively along the series 3(4). It is clear that ω_N is a measure of the instantaneous (i.e., vertical) stabilization of a given system due to a maximum charge acquisition. The difference in the pattern of

global electrophilicity of systems (3) and (4) is stressed by the direct conjugation of halogen substituent with the Si center in (3) [24], where the F atom displays the greatest effects on hardness and electrophilicity as discussed above. In particular, the electrophilicity of (4) with respect to (3) is predicted to be 1.19 (0.66), 1.03 (0.66), and 1.00 (0.72) times for F, Cl, and Br, respectively, in the singlet (triplet) electronic state. We would like to emphasize in this point that the highest electrophilicities are predicted to occur in system (2) when X = Br both in the singlet and triplet states, while the lowest ones belong to the aromatic structure (1) when X = H and the structure (4) when X = F in the singlet and triplet states, respectively. Taking the maximum differences between relative electrophilicities (i.e., relative to X = H) along the singlet ground state series, as a measure of the sensibility of chemical structure against halogen substitution [24], the predicted values for systems (1)–(4) are 0.06, 0.16, 0.19, and 0.04, respectively. That is, the allene system (2) is only 0.83 times less susceptible to halogen substitution than when a direct Si–X conjugation is present (i.e., in system (3)). This fact is in agreement with energetic results available for these systems at several level of theory [24]. The aromatic system (1) and those incorporating a triple bond are much less susceptible to such halogen substitution. This order is however inverted in the triplet state for silylenic systems (1)–(4). The predicted values are 0.12, 0.06, 0.10, and 0.16, respectively, indicating that the allene system (2) becomes strongly deactivated after excitation.

3.2. Spin polarization patterns

It has been stressed recently that the ω_S^\pm indices have to be interpreted as philicities for spin-polarization [25] and not as charge-transfer related ones as previously claimed [4,30]. Furthermore, the spin polarization processes in the studied silylenic systems can be rationalized through the examination of the spin potential μ_S^\pm and philicity ω_S^\pm as reported in Table 1. Note that a good linear correlation can be obtained between the singlet \rightarrow triplet vertical transition and these descriptors (i.e., Fig. 2). We note here that the spin potential for the triplet state, $\mu_S^{(t)-}$, turn out to be small enough (data not reported), yielding also to a linear relationship between ω_S^\pm and $-\mu_S^\pm$ along this series of silylenes in the singlet GS (see Fig. 2a). As the case for carbene related systems [4,25,30], we can note here that the philicity for spin polarization ω_S^\pm correlates in good order with the vertical transition energies [24]. Note also that within the present perturbative approximation to chemical reactivity, the relative errors in the prediction of the vertical energy gap, $\Delta E_{s \rightarrow t}^{vt}$ as the simple sum of spin potentials ($\mu_S^+ + \mu_S^{(t)-}$), becomes very small (i.e., $<1.0\%$) along the entire series of systems (1)–(4). This type of agreement is remarkable because of the simplicity of Eq. (4) used to evaluate the spin potentials.

The robustness of a linear model for the vertical transition energies and both the spin potential μ_S^\pm and philicity

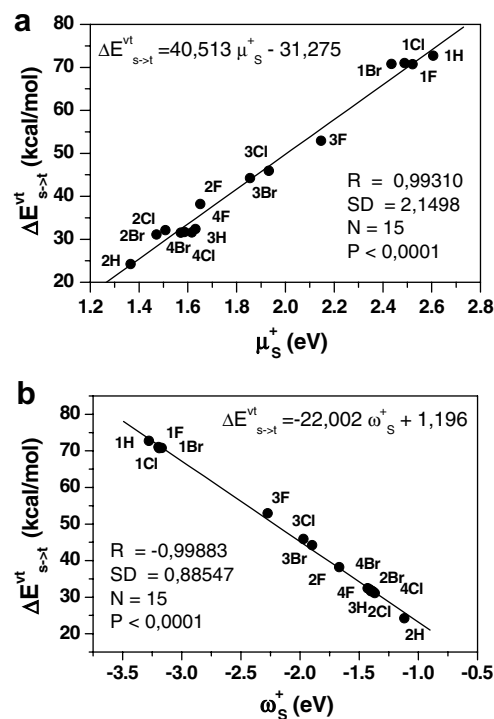


Fig. 2. Vertical triplet-singlet energy gap, $\Delta E_{s \rightarrow t}^{vt}$, for some simple silylenes vs. both (a) the spin potential, μ_S^+ and (b) the philicity for spin-polarization, ω_S^+ , R = correlation coefficient, SD = Standard deviation, N = Number of data points, and P = the test for the null hypothesis that the overall slope is zero, i.e., the probability that the correlation coefficient should be zero. The P values are obtained from the t -test of the correlation analysis. The robustness of such linear models in (a) and (b) can be easily probed through a leave-one-out cross validation analysis (see text).

for spin polarization ω_S^\pm , is evident from the statistics of the leave-one-out cross validation analysis on these data sets. Thus, the cross validation observed (y) vs. predicted (x) results for μ_S^+ (Fig. 2a) and ω_S^+ (Fig. 2b) are: $y = 0.71x + 12.4$ and $y = 1.01x - 0.544$, respectively, with $R^2 = 0.909$, adjusted $R^2 = 0.902$, the root-mean-square error of cross-validation ($RMSE$) = 6.944, the mean error (ME) = 0.592, the standard deviation error (SDE) = 7.162, and the relative percent deviation (RPD) = 2.81, for the case of μ_S^+ ; and $R^2 = 0.998$, adjusted $R^2 = 0.998$, $RMSE = 0.935$, $ME = -0.077$, $SDE = 0.965$, $RPD = 20.86$, for the case of ω_S^+ . The results for the philicity ω_S^\pm show it as a better descriptor in such a context.

3.3. Local reactivity (spin polarization)

Concerning local aspects of chemical reactivity [26], the results based on the Fukui functions reported in Table 2 show that under a spin polarization process, the greatest charge and spin density changes should be in fact [24] practically centered on the Si atom (i.e., $f_{NS, Si}^+ > 0$, and $f_{SS, Si}^+ > 0$). Note from Table 2, that our simple model implementation for the evaluation of condensed-to-site Fukui functions [25], predicts that charge density (and spin density) accumulation (depletion) are inversely (directly)

Table 2
 SP-DFT $f_{NS,k}^+$ and $f_{SS,k}^+$ Fukui functions for substituted silylene systems in their singlet ground state in Fig. 1

(1H)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(2H)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(3H)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(4H)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$
1	C	-0.0602	0.1233	1	C	0.1282	0.1414	1	C	0.0053	0.1722	1	C	0.0053	0.1722
2	C	-0.0602	0.1233	2	H	-0.0169	0.0169	2	H	-0.0001	0.0001	2	C	-0.2910	0.0381
3	H	-0.0005	0.0005	X	H	-0.0169	0.0169	3	C	-0.2910	0.0381	3	Si	0.0980	0.7155
X	H	-0.0005	0.0005	4	C	-0.2178	0.2470	4	Si	0.0980	0.7155	4	H	-0.0741	0.0741
5	Si	0.1213	0.7524	5	Si	0.1233	0.5779	X	H	-0.0741	0.0741	X	H	-0.0001	0.0001
(1F)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(2F)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(3F)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(4F)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$
1	C	-0.0176	0.1321	1	C	0.1129	0.1410	1	C	0.0492	0.1239	1	C	0.0046	0.1423
2	C	-0.0866	0.1180	2	H	-0.0105	0.0105	2	H	-0.0008	0.0008	2	C	-0.0352	0.0391
3	H	-0.0026	0.0026	X	F	0.0067	0.0314	3	C	-0.0616	0.0829	3	Si	0.1104	0.7193
X	F	-0.0341	0.0388	4	C	-0.2644	0.2736	4	Si	0.0267	0.7233	4	H	-0.0763	0.0763
5	Si	0.1409	0.7085	5	Si	0.1553	0.5435	X	F	-0.0134	0.0691	X	F	-0.0034	0.0231
(1Cl)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(2Cl)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(3Cl)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(4Cl)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$
1	C	-0.0159	0.0915	1	C	0.1209	0.1341	1	C	0.0479	0.1205	1	C	0.0045	0.1592
2	C	-0.0829	0.1310	2	H	-0.0117	0.0117	2	H	-0.0006	0.0006	2	C	-0.0338	0.0432
3	H	-0.0039	0.0039	X	Cl	-0.0129	0.0545	3	C	-0.0467	0.0601	3	Si	0.1154	0.6826
X	Cl	-0.0881	0.0959	4	C	-0.2405	0.2622	4	Si	0.0683	0.6847	4	H	-0.0723	0.0723
5	Si	0.1908	0.6778	5	Si	0.1442	0.5375	X	Cl	-0.0689	0.1341	X	Cl	-0.0138	0.0428
(1Br)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(2Br)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(3Br)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$	(4Br)	Atom	$f_{NS,k}^+$	$f_{SS,k}^+$
1	C	-0.0051	0.0781	1	C	0.1202	0.1302	1	C	0.0535	0.1119	1	C	0.0054	0.1575
2	C	-0.0721	0.1220	2	H	-0.0112	0.0112	2	H	-0.0005	0.0005	2	C	-0.0360	0.0447
3	H	-0.0045	0.0045	X	Br	-0.0297	0.0760	3	C	-0.0396	0.0523	3	Si	0.1224	0.6705
X	Br	-0.1519	0.1609	4	C	-0.2260	0.2469	4	Si	0.0931	0.6429	4	H	-0.0709	0.0709
5	Si	0.2336	0.6346	5	Si	0.1467	0.5356	X	Br	-0.1064	0.1924	X	Br	-0.0209	0.0565

related to the electronegativity character of substituent along the singlet ground state series. Being the hydrogen atom the reference system, note that such a accumulation (depletion) of charge (spin) density at Si occurs by factors of 1.16 (0.94), 1.57 (0.90), and 1.93 (0.84) times for F, Cl, and Br in the system (1); 1.26 (0.94), 1.17 (0.93), and 1.19(0.93) in system (2); 0.27(1.01), 0.70 (0.96), and 0.95 (0.90) in system (3); and 1.13 (1.00), 1.18 (0.95), and 1.25 (0.94) in system (4). Note also that direct halogen substitution on the silylenic center in system (3), in contrast to (4), is predicted to strongly reduce the charge accumulation in such a center by factors of 4.13, 1.69, and 1.31 times, for F, Cl, and Br, respectively. Because spin density remains unaffected, it is clear that conjugation of halogen lone pairs with Si center becomes active in system (3) [24]. Note also that charge (spin) accumulation on the closets carbon centers allows a better interaction between the halogen and the reactive center on the Si atom. Hence, it is clear from the pattern of charge (spin) accumulation in the carbon atoms directly bonded to Si atom in systems (2) and (4), that such a substituent effect under a spin polarization process is stronger (i.e., more effective) through double than triple bonds [24]. Our reactivity models assess for these effects.

4. Concluding remarks and perspectives

The electrophilicity patterns of some simple silylene systems have been further characterized in the context of global and local electrophilicity indices recently introduced [25] within a spin polarized DFT framework. Both philicity

for spin polarization, ω_S^\pm , as well as charge transfer at constant spin number, ω_N , provides complementary information for a comprehensive description of both global and local chemical reactivity patterns and halogen substituent effects in these systems [24].

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